

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 27/32	A1	(11) International Publication Number: WO 99/10172 (43) International Publication Date: 4 March 1999 (04.03.99)
(21) International Application Number: PCT/US98/14820 (22) International Filing Date: 17 July 1998 (17.07.98) (30) Priority Data: 08/918,172 25 August 1997 (25.08.97) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventors: CHU, Shaw-Chang; 3 Wynwood Drive, Princeton Junction, NJ 08550 (US). HEFFELFINGER, Michael, Thomas; 5423 Garnier Place, Westerville, OH 43081-8612 (US). KEUNG, Jay, Kin; 22 Jalan Tupai, Singapore 249149 (JP). PEET, Robert, Guthrie; 44 Sunset Boulevard, Pittsford, NY 14534-2143 (US). (74) Agents: SINNOTT, Jessica, M. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		(81) Designated States: AU, BR, CA, CN, ID, JP, KR, SG, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: MULTI-LAYER FILMS WITH SYNDIOTACTIC BARRIER LAYER CONTAINING A WAX (57) Abstract An oriented multilayer film which comprises: (a) at least one layer comprising an olefin polymer such as isotactic polypropylene, and (b) a barrier layer adjacent layer (a) comprising a syndiotactic polypropylene homopolymer and at least 10% of a wax material such as polyethylene wax having a molecular weight in the range of 300-800 and a melting point between 52-72 deg. C.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

MULTI-LAYER FILMS WITH SYNDIOTACTIC BARRIER LAYER CONTAINING A WAX

The invention relates to a barrier film which comprises oriented polypropylene. A barrier layer improves moisture barrier properties and reduces oxygen transmission.

Oriented polypropylene films are known for use in packaging operations. U.S. Patent No. 4,604,324 to Nahmias et al., discloses multi-layer polypropylene film structure comprising coextruded
5 layers of a base layer of high stereoregularity polypropylene and a skin layer of comparatively low stereoregularity which contains anti-stick additives. In addition, the skin layer can contain up to 10 weight percent (wt.%) of a wax to improve heat seal characteristics or optical properties of the film. U.S. Patent No. 5,254,394 to Bothe et al., discloses a polyolefin film for packaging comprising isotactic polypropylene base layer and a top layer of syndiotactic polypropylene which has high sealed-seam
10 strength and excellent optical properties. The layers may contain lubricant additives such as waxes at levels of up to 2 wt.%, relative to each layer.

U.S. Patent No. 5,155,160 to Yeh et al., discloses improving barrier properties of crystalline or isotactic polyolefin films by incorporating 3 to 10 wt.% wax, such as paraffin wax in the isotactic polyolefin. The reference discloses affecting barrier properties by modifying chill roll conditions.

15 The invention relates to a multi-layer film which can provide an effective moisture and oxygen barrier without requiring such barrier agents as polyterpenes, alicyclic hydrocarbons, or high barrier polyvinylidene chloride coatings.

The invention relates to an oriented multi-layer film which comprises:

- (a) at least one layer comprising an olefin polymer, and
- 20 (b) a barrier layer adjacent layer (a) comprising a syndiotactic polypropylene homopolymer, which possesses isotacticity of less than 25%, and moisture and oxygen permeability reducing amounts of wax. More particularly, the (a) layer is different from the (b) layer.

The invention further relates to an oriented multilayer film comprising a syndiotactic propylene polymer and an amount of wax sufficient to achieve a water vapor transmission rate of less than 0.2,
25 specifically less than 1.6 g/100 in²/mil/day at 38°C and 90% relative humidity.

Alternatively, the invention is directed to a process for preparing an oriented multi-layer film which comprises melt coextruding a combination comprising:

- (a) at least one layer comprising an olefin polymer, and
- 30 (b) a barrier layer adjacent layer (a) comprising a syndiotactic polypropylene homopolymer, which possesses isotacticity of less than 25%, and moisture and oxygen permeability reducing amounts of wax;

and orienting said coextruded combination.

Layer (a)

At least one layer (a), of the multi-layer film comprises an olefin polymer such as a propylene polymer which is preferably predominantly (at least 90% by weight) comprised of propylene and preferably has a melting point of 140°C or higher, more preferably a melting point of 150°C or higher.

Isotactic polypropylene having an n-heptane soluble content of 15% by weight or less, copolymers of ethylene and propylene having an ethylene content of 10% by weight or less, and copolymers of polypropylene and (C₄-C₈) alpha-olefins having a (C₄-C₈) alpha-olefin content of 10% by weight or less are preferred examples of the olefin polymer used for the base layer.

The propylene polymer of the layer (a) preferably has a melt flow index of 0.5 g/10 min to 8 g/10 min, more preferably, 1.5 g/10 min to 4 g/10 min, at 230°C and at a load of 21.6 N (DIN 53735). Examples of such layer (a) propylene polymers include Fina 3371 (commercially available from Fina Oil and Chemical Company, and PP 4252 (commercially available from Exxon Corporation).

Barrier Layer

The barrier layer contains a syndiotactic polypropylene blended with a wax component. The syndiotactic polypropylene preferably possesses an isotacticity of less than 25%, in particular less than 6%. The mean length of sequence n, of the syndiotactic sequences is preferably greater than 20, more preferably greater than 25. The molar mass distribution corresponds to the relation

$$M_w = k \times M_n,$$

where

M_w stands for the weight average of the molar mass distribution,

M_n stands for the number average of the molar mass distribution and

k is a factor which is between 1 and 5, preferably between 2 and 3.

The weight average is preferably between 60,000 and 250,000, in particular between 90,000 and 160,000. The mean molar masses can be determined according to customary methods; of these, the method of gel permeation chromatography has proven to be particularly suitable.

Syndiotactic polypropylene resins suited to use in the present invention include EOD 93-06 and EOD 95-01, available from Fina Oil and Chemical Company.

The wax used is typically a hydrocarbon wax, which may be either a mineral wax or a synthetic wax. Polyethylene type wax is especially preferred which has an average chain length between 22 and 65 carbon atoms, a molecular weight between 300 and 800, and a melting point between 125° and 190°F (52° and 88°C). These waxes include paraffin waxes, microcrystalline waxes, and intermediate waxes. Most preferred are paraffin waxes, which typically have an average chain length between 22 and 40

carbon atoms, a molecular weight between 300 and 450, and a melting point between 125° and 160°F (52° and 71°C). The paraffin wax typically consists of a mixture of normal and branched paraffins, with the normal paraffin content preferably being from 35 to 90% by weight. The paraffin wax typically has a broad molecular weight distribution. For example, each fraction of chains containing a certain number of carbon atoms preferably represents less than 25%, more preferably less than 20%, of the wax. A paraffin wax having a broad molecular weight distribution provides better barrier properties than a paraffin wax having a narrow molecular weight distribution, which is believed to be due to the formation by the wax having the broad molecular weight distribution of crystallites that have a morphology that conforms better with the morphology of the amorphous regions of the polyolefin. A particularly suitable wax is Chevron 143. It has a melting point of 143°F (62°C), an average chain length of 29 carbon atoms, an average molecular weight of 416, a normal paraffin content of 74%, and contains 12% C₂₈ fraction, 12% C₂₉ fraction, and 11% C₃₀ fraction (the three largest fractions in the wax).

Wax is added to the syndiotactic polypropylene in amounts which reduce water vapor transmission rate (WVTR) and oxygen transmission (TO₂) of the resulting film product. For present purposes, WVTR can be measured at 100°F (38°C) and 90% relative humidity in accordance with ASTM E96 and TAPPI Standard T464. TO₂ is measured in accordance with ASTM D 3985-81 (cc/100 in²/24 h). Generally, the amount of wax added to the barrier layer can depend on the amorphousness of the polyolefin, which in turn can depend on the type of polyolefin, the method of cooling the extruded film containing the polyolefin, and the thickness of the film. Typically, the barrier layer contains greater than 10 wt.% wax, specifically at least 12 wt.% wax, say, at least 15 wt.% wax.

Usually, the wax-containing barrier layer is not an exposed surface in order to avoid wax blooming to the surface. Accordingly, the barrier layer is often sandwiched between a core layer and an outer skin layer. In another embodiment, the barrier layer forms the core of a multilayer film.

Outer Layer

An outer layer of the present invention may be any of the coextrudable, biaxially orientable film-forming resins known. Such materials include those discussed above which are suitable for use in the (a) layer, including isotactic polypropylene, polypropylene blended with polybutene-1, and ethylene-propylene copolymer, including fractional ethylene-propylene copolymer. Suitable ethylene-propylene copolymers include ethylene-propylene random copolymer and ethylene-propylene block copolymer. In addition, polyethylene, polybutene-1, ethylene-propylene-butene-1 terpolymer, polyester, nylon, ethylene-vinyl-acetate, and ethylene vinyl- alcohol may be employed as the outer layer. In one embodiment, the skin layer can be identical in composition to the (a) layer.

Ethylene-propylene-butene-1 random terpolymers appropriate for use in the outer layer of the present invention include those containing 1 to 5 wt.% random ethylene, and 5 to 25 wt.% random butene-1. The amounts of the random ethylene and butene-1 components in these copolymers are typically in the range of 10 to 25% (ethylene plus butene-1) based on the total amount of the copolymer.

5 These copolymers typically have a melt flow rate in the range of 5 to 10, with a density of 0.9, and a melting point in the range of 115° to 130°C.

In one aspect of the invention the outer layer is derived from a low density polyethylene. This may be a linear low density polyethylene (LLDPE) or a standard low density polyethylene. These polymers typically have a melt index of 0.5 to 10. The low density polyethylenes should have a density
10 of 0.88 to 0.93 while the linear materials may have a density as high as 0.94, usually in the range 0.90 to 0.94, e.g. 0.918 or 0.921, with a melt index from 1 to 10. The linear low density polyethylenes may be derived from ethylene together with other higher comonomers such as butene-1, hexene-1 or octene-1.

Each outer layer can range in thickness from 0.5 to 3 microns, preferably 0.5 to 1.0 micron, e.g., 0.5 to 0.75 micron.

15 Additives

In order to further improve certain properties of the multi-layer films of the invention, it is possible for one or more of the layers to contain appropriate additives in an effective amount. Preferred additives include antistatic agents, antiblocking agents, lubricants, stabilizers, and/or low molecular weight resins. Such additives are further described in U.S. Patent No. 5,254,394.

20 Surface Treating

One or more of the exposed layers of the multi-layer films of the present invention can be surface-treated to render them receptive, e.g., to printing inks. The surface treatment can be carried out according to one of the methods known in the art. Methods which are known include, e.g., electrical spray discharge between two electrodes, i.e., corona treatment, flame treatment, or treatment by means of
25 a polarized flame.

Coating

The syndiotactic polypropylene/wax barrier layer of the present invention provides multi-layer films of high moisture barrier and high oxygen transmission barrier without requiring the use of barrier coatings whose presence can often cause difficulties in product recycling. However, where necessary,
30 moisture barrier capability may be further enhanced by techniques such as coating with acrylic polymers, polyvinylidene chloride (PVDC) or poly(vinyl)alcohol.

Acrylic coatings can be derived from any of the terpolymeric compositions disclosed in U.S. Patent Nos. 3,753,769 and 4,865,908. These coating compositions contain as a film forming component

a resin consisting essentially of an interpolymers of (a) from 2 to 15, and preferably from 2.5 to 6, parts by weight of an alpha-beta monoethylenically unsaturated carboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof, and (b) from 85 to 98, and preferably from 94 to 97.5, parts by weight of neutral monomer esters, said neutral monomer esters preferably comprising (1) methyl acrylate or ethyl acrylate and (2) methyl methacrylate. These interpolymers compositions are further characterized by preferably comprising from 30 to 55% by weight of methyl methacrylate when said alkyl acrylate is methyl acrylate, and from 52.5 to 69% by weight of methylmethacrylate when said alkyl acrylate is ethyl acrylate. As more fully described infra, such coating compositions can be applied to the films herein in a variety of ways including in the form of ammoniacal solutions.

Similarly useful are copolymeric coating compositions prepared from the foregoing neutral monomer esters. These coating compositions are advantageously applied to the film laminates in the form of emulsions.

The coating can also be based on any of the known and conventional polyvinylidene chloride (PVDC) compositions heretofore employed as coatings in film manufacturing operations, e.g., any of the PVDC materials described in U.S. Patent Nos. 4,214,039; 4,447,494; 4,961,992; 5,019,447 and 5,057,177.

U.S. Patent No. 5,230,963 discloses enhancing oxygen barrier of films by a method involving a coating, preferably with prior application of a primer layer to enhance adhesion of the PVDC coating layer to the film surface to which it is applied. Commercially available PVDC latexes having a vinylidene chloride content of at least 50% and preferably from 75 to 92% may be employed. The PVDC can also be provided as a copolymer of vinylidenechloride and one or more other ethylenically unsaturated comonomers including alpha, beta ethylenically unsaturated acids such as acrylic and methacrylic acids; alkyl esters containing 1 to 18 carbon atoms of said acids, such as methylmethacrylate, ethyl acrylate, butyl acrylate, etc. In addition alpha, beta ethylenically unsaturated nitriles such as acrylonitrile and methacrylonitrile and monovinyl aromatic compounds such as styrene and vinyl chloride comonomers can be employed. Specific PVDC latexes contemplated comprise 82% by weight vinylidene chloride, 14% by weight ethyl acrylate and 4% by weight acrylic acid. Alternatively, a polymer latex comprising 80% by weight vinylidene chloride, 17% methyl acrylate and 3% by weight methacrylic acid, can likewise be employed.

The vinyl alcohol polymers which may be used as coatings can be any commercially available material. For example, Vinol 125, 99.3 +% super hydrolyzed polyvinyl alcohol, or Vinol 325, 98%

hydrolyzed polyvinyl alcohol obtained from Air Products, Inc. Application of a PVOH coating is further described in U.S. Patent No. 5,230,963.

Before applying the coating composition to the appropriate substrate, the upper surface of the film is preferably treated as noted above to increase its surface energy and therefor insure that the coating layer will be strongly adherent thereto thereby reducing the possibility of the coating peeling or being stripped from the film. This treatment can be accomplished employing known techniques, such as, for example, film chlorination, i.e., exposure of the film surface to gaseous chlorine, treatment with oxidizing agents such as chromic acid, hot air or steam treatment, flame treatment and the like. Although any of these techniques is effectively employed to pretreat the film surface, a particularly desirable method of treatment is the so-called electronic treatment method which comprises exposing the film surface to a high voltage corona discharge while passing the film between a pair of spaced electrodes. After electronic treatment of the film surface, the coating composition is then applied thereto.

In applications where even greater coating-to-film adherence is desired, i.e., greater than that resulting from treatment of the film surface by any of the aforescussed methods, an intermediate primer coating can be employed to increase the adherence of the coating composition to the film. In this case, the film is advantageously first treated by one of the foregoing methods to provide increased active adhesive sites thereon (thereby promoting primer adhesion) and to the thus treated film surface there is subsequently applied a continuous coating of a primer material. Such primer materials are well known in the prior art and include, for example, epoxy and poly(ethylene imine) (PEI) materials. U.S. Patent Nos. 3,753,769 and 4,058,645 to Steiner, and 4,439,493 to Hein et al., disclose the use and application of such primers. The primer provides an overall adhesively active surface for thorough and secure bonding with the subsequently applied coating composition and can be applied to the film by conventional solution coating means, for example, by mating roller application.

The coating composition can be applied to the film as a solution, e.g., one prepared with an organic solvent such as an alcohol, ketone, ester, etc. However, since the coating composition can contain insoluble, finely divided inorganic materials which are difficult to keep well dispersed in organic solvents, it is preferable that the coating composition be applied to the treated surface in any convenient manner, such as by gravure coating, roll coating, dipping, spraying, etc. The excess aqueous solution can be removed by squeeze rolls, doctor knives, etc.

The film can be stretched in the machine direction, coated with the coating composition and then stretched perpendicularly in the transverse direction. In yet another embodiment, the coating can be carried out after biaxial orientation is completed. Biaxially oriented film is typically stretched 4.5 to 6

times in the machine direction (MD), and 6 to 13 times in the transverse direction (TD). The overall orientation (MD X TD) can range from 25 to 80.

The coating composition should be applied in such amount that there will be deposited upon drying a smooth, evenly distributed layer, generally on the order of from 0.01 to 0.2 mil (0.25 to 5.08 microns) thickness (equivalent to 0.2 to 3.5 g per 6451.6 cm² of film). In general, the thickness of the applied coating is such that it is sufficient to impart the desired seal peelability, oxygen and water vapor barrier characteristics to the resulting film. Generally, the coating comprises 1 to 25 wt.%, preferably 7 to 15 wt.% of the entire coated film composition. The coating on the film is subsequently dried by hot air, radiant heat or by any other convenient means.

In each of the examples, the barrier properties of the films were tested by the following methods.
Examples 1 to 3

Five-layer multi-layer films of the present invention were prepared employing commercially available systems for coextruding resins. Each multi-layer film had the structure ABCBA where A is the skin layer, B is the barrier layer, and C is the base layer. The base layer used in all three examples was Fina 3371, a conventional isotactic homopolymer of propylene. The barrier layers were syndiotactic polypropylene (EOD 9306) 15 wt.% wax being added to the syndiotactic polypropylenes in Examples 2 and 3. The skin layers were an ethylene-propylene terpolymers (XPM 7702), available from Chisso for Example 1, Z9470 and 8573HB, available from Fina, for Examples 2 and 3, respectively.

The multi-layer films of the Examples were prepared as follows:

The polymers were brought to the molten state and coextruded from a conventional extruder through a flat sheet die, the melt streams being combined in an adapter prior to being extruded from the die. After leaving the die, the multi-layer film structure is chilled and the quenched sheet then reheated and oriented.

The film was biaxially oriented. After orientation, the edges of the film were trimmed and the film wound into a roll.

In general, the total film thickness of the multi-layer film structure having a structure which can be illustrated by layers ABCBA where layer A is an outer layer, layer B is an intermediate layer and layer C is a core layer. The barrier layer of this invention is, typically, employed in layer B or C. The film is usually from 10µm, to 64µm, preferably from 12µm to 50µm. The thickness relationship of the layers is sometimes important. In particular, the B layers are provided as a relatively thick layer of 5 to 40% of the total thickness of the film with from 10 to 25% being preferred. The A layer is advantageously from 1µm to 5µm in thickness when the total film is, for example, 0.8 mil (20.32 microns) thick.

The core layer, C is advantageously from 40 to 95% of the total thickness of the film, preferably from 50 to 85%.

The data in the Table below show the benefits of the film made according to the invention. Examples 2 and 3 are compositions in accordance with the invention and show improvement over Example 1 (Comparative) in water vapor transmission (WVTR).

The film of Example 2 had a "C" layer thickness of 29 microns, each "B" layer had a thickness of 4.3 microns, and each "A" layer had a thickness of 1.3 microns to provide a film of 40.2 microns.

The film of Example 3 had a "C" layer thickness of 28.7 microns, each "B" layer had a thickness of 2.9 microns and each "A" layer had a thickness of 0.99 microns to provide a film of 36.5 microns.

TABLE

Wax (Wt.%)	Example No.	WVTR ¹		
		Total	Ambient	OTR ²
0	1		0.365	
15	2	1.58	0.13	21.2*
15	3	1.44	0.112	22.5*

Note: 1. WVTR = gm/645.16 cm² /25.4 microns/day measured at 38°C & 90% relative humidity

2. OTR* = cc/645.16 cm² /day at 1 atm, 23°C & 0% relative humidity

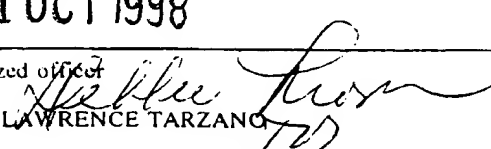
* The OTR of conventional polypropylene is typically 150 cc/645.16 cm² /day at 1 atm, 23°C and 0% relative humidity.

CLAIMS:

1. An oriented multi-layer film which comprises:
 - (a) at least one layer comprising an olefin polymer, and
 - (b) a barrier layer adjacent the (a) layer comprising a syndiotactic propylene homopolymer,
- 5 which possesses isotacticity of less than 25%, and moisture and oxygen permeability reducing amounts of wax in an amount of at least 10% wax.
2. The multi-layer film of claim 1 which further comprises:
 - (c) a skin layer adjacent the barrier layer comprising polyolefin.
3. The multi-layer film of claim 1 which further comprises:
 - (c) an outer layer adjacent the barrier layer comprising polyolefin selected from the group consisting of isotactic polypropylene, ethylene-propylene random copolymer, ethylene-propylene block copolymer, ethylene-propylene-butene-1 copolymer, polybutene-1, polyester, nylon, ethylene vinyl
 - 5 acetate and ethylene vinyl alcohol.
4. The oriented multi-layer film of claim 3 wherein the outer layer (c) is coated with a coating selected from the group consisting of polyvinylidene chloride, polyvinyl alcohol, and acrylic.
5. The oriented multi-layer film of claim 1 wherein the wax of barrier layer (b) is a polyethylene type wax having an average chain length between 22 and 65 carbon atoms, a molecular weight between 300 and 800, and a melting point between 52° and 71°C.
6. An oriented multilayer film comprising at least one barrier layer comprising a syndiotactic propylene polymer and an amount of wax sufficient to achieve a water vapor transmission rate of less than 0.2 g/645.16 cm²/25.4 microns/day at 38 and 90% relative humidity.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/14820

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : B32B 27/32 US CL : 428/35.5, 484, 515, 516, 910 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 428/35.5, 484, 515, 516, 910 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched none Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS: syndiotactic polypropylene, wax, multilayer films.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,141,801 A (TAKESHITA et al.) 25 August 1992, see the entire document especially column 1, lines 47-65; column 2, lines 10-14; column 4, lines 17-25; and the claims.	1-6
Y	US 4,892,851 A (EWEN et al.) 9 January 1990, see column 2, line 23+.	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* "A" "E" "L" "O" "P"	Special categories of cited documents. Document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family
Date of the actual completion of the international search 24 AUGUST 1998		Date of mailing of the international search report 21 OCT 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  D. LAWRENCE TARZANO Telephone No. (703) 308-2379